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## Examination of methods to measure capillary threshold pressures of pelitic rock samples

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### Abstract

In this work we have examined measurement methodologies of capillary threshold pressure and effects of injected fluid differences. Firstly N<sub>2</sub> gas capillary threshold pressures were directly measured with selected pelitic rock sample using two approaches; step-by-step approach and residual pressure approach. Capillary threshold pressures with these two approaches show different values within the same core sample. Values with residual pressure approach are always lower than those with step-by-step approach. Secondly this pelitic rock sample was also applied for different injected fluids with step-by-step approach; N<sub>2</sub> gas and supercritical CO<sub>2</sub> were injected. This experiment shows that the measured value of threshold capillary pressure for supercritical CO<sub>2</sub> is smaller by two-thirds than that for N<sub>2</sub> gas. This result also suggests that the measured capillary threshold pressure for supercritical CO<sub>2</sub> is larger than the recalculated value from N<sub>2</sub> gas data with the Laplace equation.

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### 1. Introduction

Greenhouse gases, like carbon dioxide (CO<sub>2</sub>), are regarded to affect temperature of the earth and cause global warming. CO<sub>2</sub> Capture and Storage (CCS) within the deep saline aquifer or the depleted reservoir seems at present to be the most promising approach. The caprock formations overlying the injection unit

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play an important role in avoiding CO<sub>2</sub> leakage. Therefore to understand the caprock seal capacities is of great significance for evaluating storage capacity during geological storage.

Measurement of capillary threshold pressure is one of the most effective methods to know the sealing ability of caprocks and has been conducted directly/indirectly by many researchers [1] [2] [3].

Conventional High Pressure Mercury Injection (HPMI) is an indirect method and used to anticipate the magnitude of capillary threshold pressure [2]. Step-by-step approach is a direct measuring method. This approach is time consuming but it is the most reliable approach. Residual pressure approach is proposed recently and considered to provide underestimated values of capillary threshold pressure compared to step-by-step approach [3].

The objective of this study is to compare these approaches and to develop the most effective way of measuring capillary threshold pressure with pelitic rock samples.

## 2. Experimental approach

### 2.1. Pelitic rock samples

One mudrock (pelitic) core from the Japanese oil/gas field was supplied as an experimental caprock sample soaked with formation water and wrapped to keep wet conditions. From this mudrock core, one core plug was drilled and formed into 4.1 cm length and 3.6 cm diameter. Core plug was saturated with brine (28,000 mg/L-NaCl) and applied to the following experiments; residual pressure approach for N<sub>2</sub> gas, step-by-step approach for N<sub>2</sub> gas and step-by-step approach for supercritical CO<sub>2</sub> in order. Preliminary to each approach, water (brine) permeability was measured to saturate this sample with brine completely and to confirm that no alteration of pore structure had occurred in previous experiments.

Also two fragments from the same location where core plug has been drilled were taken as samples and then, cleaned and dried for preparation. These fragments were applied to HPMI measurements which gave porosity data and pore size distributions (Table 1).

Table 1. Overviews of samples

Sample no.	Sample type	Rock type	Depth (m)	Porosity (%)	Experimental Item
1-a, a'	Fragments	Mudrock	1404.59~.65	30.4	HPMI
1-b	Core plug	Mudrock	1404.60~.64	-	Kw, Pc(threshold, N <sub>2</sub> gas) with residual pressure Pc(threshold, N <sub>2</sub> gas) with step-by-step Pc(threshold,sc-CO <sub>2</sub> ) with step-by-step

### 2.2. Anticipation from High Pressure Mercury Injection (HPMI)

The pore size distribution of sample 1-a derived by HPMI is shown in Figure 1. The value of capillary threshold pressure (Pc<sup>th</sup>) with mercury/air fluids system can be considered as a point of mercury capillary pressure (Pc) at 10% pore volume occupied with mercury. The relational expression between pore throat radius and mercury capillary pressure (Pc) is given by the Laplace equation below;

$$P_c = \frac{2\sigma \cos \theta}{R_{\text{throat}}} \quad (1)$$

Where  $P_c$  (MPa) is capillary pressure calculated from HPMI,  $\sigma$  (mN/m) is interfacial tension,  $\theta$  ( $^\circ$ ) is contact angle and  $R_{\text{throat}}$  is throat radius (nm). In sample 1-a,  $P_c$  for mercury/air is 6.75 MPa and considered as a capillary threshold pressure ( $P_c^{\text{th}}$ ). This value is available to anticipate capillary threshold pressure for  $N_2$ /brine and for  $CO_2$ /brine by using the following equation which is based on the Laplace equation.

$$P_{c(\text{gas/brine})}^{\text{th}} = -P_{c(\text{Hg/air})}^{\text{th}} \frac{\sigma_{\text{gas/brine}} \cos \theta_{\text{gas/brine}}}{\sigma_{\text{Hg/air}} \cos \theta_{\text{Hg/air}}} \quad (2)$$

The values of interfacial tension (IFT) and contact angle for  $CO_2$ /brine fluids system under near-experimental conditions are chosen from the published data [4] [5] and given in Table 2.

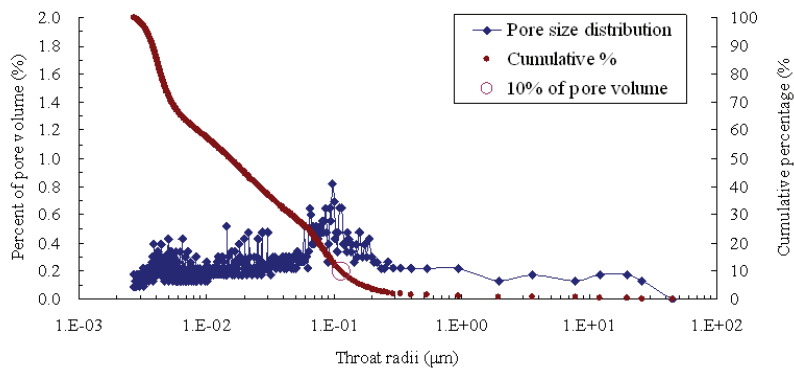


Fig. 1. Pore size distribution by HPMI (sample 1-a)

Table 2. Interfacial tension (IFT) and contact angle values chosen for anticipation

	Hg/air	$N_2$ /brine	Supercritical $CO_2$ /brine
Interfacial tension (mN/m)	480	72	27
Contact angle ( $^\circ$ )	140	0	34

### 2.3. Residual pressure approach for $N_2$ gas

Residual pressure approach was proposed recently [3]. Core plug saturated with brine was placed into a coreholder. Net confining pressure of about 10MPa for reflecting *in-situ* condition was applied to core plug (Figure 2-a). Prior to capillary threshold pressure measurements, water (brine) permeability was measured. High  $N_2$  gas pressure was applied and pressure changes ( $P_{\text{out}}$ ) in a closed downstream chamber were monitored.

The downstream pressure normally increases as a function of elapsed-time. After a pressure equilibration, the residual pressure ( $P_{\text{in}} - P_{\text{out}}$ ) shows a characteristic parameter for a sample. This residual pressure is assumed as a capillary threshold pressure.

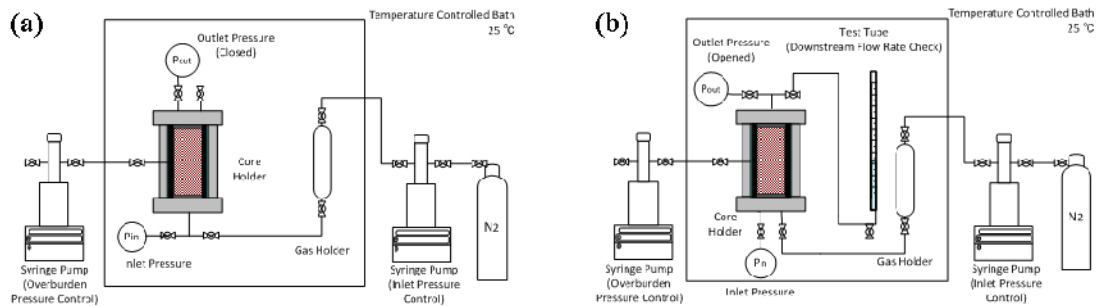


Fig. 2 Schematic apparatus for  $N_2$  gas, (a) residual pressure approach, (b) step-by-step approach

#### 2.4. Step-by-step approach for $N_2$ gas

Core sample was set into a coreholder and added net confining pressure. Before injecting  $N_2$  gas, stable water permeability was measured. Initially  $N_2$  gas was injected at inlet to displace brine. In a stepwise manner, inlet  $N_2$  gas pressure increased by 0.17 MPa increments and very small movements of downstream brine in an opened test tube were monitored (Figure 2-b). This procedure was repeated until continuous flow of downstream brine was observed. The inlet gas pressure of the last step was regarded as a capillary threshold pressure.

#### 2.5. Step-by-step approach for supercritical $CO_2$

Step-by-step approach for supercritical  $CO_2$  is required a temperature-controlled and high pressure-controlled system to keep  $CO_2$  in its supercritical state.  $CO_2$  behaves as a supercritical fluid above its critical temperature (31.1 °C) and its critical pressure (7.39 MPa). In this experiment, the system was kept at 40 °C and above 10MPa condition. Core sample was set up like those above. A backpressure pump was placed instead of a test tube and kept constant downstream pressure of brine at 10 MPa. Under backpressure of 10 MPa and 40 °C conditions, water permeability measurement and step-by-step approach were conducted (Figure 3). Inlet  $CO_2$  pressure was increased by 0.07 MPa increments for each step and the downstream flow was monitored by a backpressure pump.

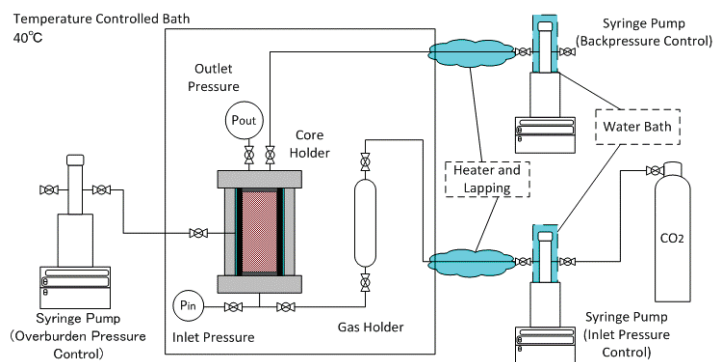


Fig. 3. Schematic apparatus with step-by-step approach for supercritical  $CO_2$

### 3. Results

#### 3.1. Threshold capillary pressure anticipation by HPMI

Table 3 summarized the anticipated value of capillary threshold pressure from HPMI. The anticipated  $P_c^{\text{th}}$  for supercritical  $\text{CO}_2$  was smaller by approximately one-third than the  $P_c^{\text{th}}$  for  $\text{N}_2$  gas.

Sometimes, fragments sampled from the same core give different distribution curves because of its heterogeneity. In this experiment, however, two fragments had very similar and normal-distributed curves. In table3, values of  $P_c^{\text{th}}$  for mercury/air from two samples are close.

Table 3. Threshold capillary pressure anticipation from HPMI

Sample no	$P_c^{\text{th}}$ mercury/air (MPa)	$P_c^{\text{th}}$ $\text{N}_2$ /brine (MPa)	$P_c^{\text{th}}$ $\text{CO}_2$ /brine (MPa)
1-a	6.75	1.30	0.40
1-a'	6.99	1.35	0.42

#### 3.2. Threshold capillary pressure with residual pressure and step-by-step approach for $\text{N}_2$ gas

Capillary threshold pressure measurements for  $\text{N}_2$  gas were conducted using two methods; residual pressure approach and step-by-step approach. The test histories of  $\text{N}_2$  gas capillary threshold pressure measurements are given in Figure 4-a and 4-b (sample 1-b).

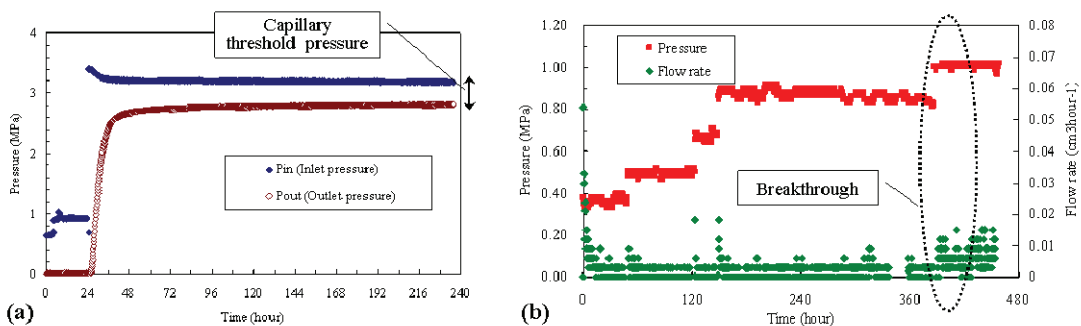


Fig. 4. Test history of  $\text{N}_2$  gas capillary threshold pressure measurements (sample 1-b), (a) residual pressure approach, (b) step-by-step approach

In figure 4-a, the inlet  $\text{N}_2$  gas pressure ( $P_{\text{in}}$ ) decreased and the outlet pressure ( $P_{\text{out}}$ ) increased with time. After a certain lag time, the residual pressure difference ( $P_{\text{in}} - P_{\text{out}}$ ) reached an equilibrium state. This residual pressure was regarded as a capillary threshold pressure.

In figure 4-b, initially, a trace production of brine at outlet was observed after each inlet pressure increment. The injection pressure was increased to the next level when the downstream flow ceased or the downstream flow rate dropped below  $0.005 \text{ cm}^3/\text{hour}$ . At inlet pressure of about 1.0 MPa, a continuous and marked increasing flow was observed on a downstream side.  $\text{N}_2$  gas capillary threshold pressure of sample 1-b was considered between 0.9 and 1.0 MPa.

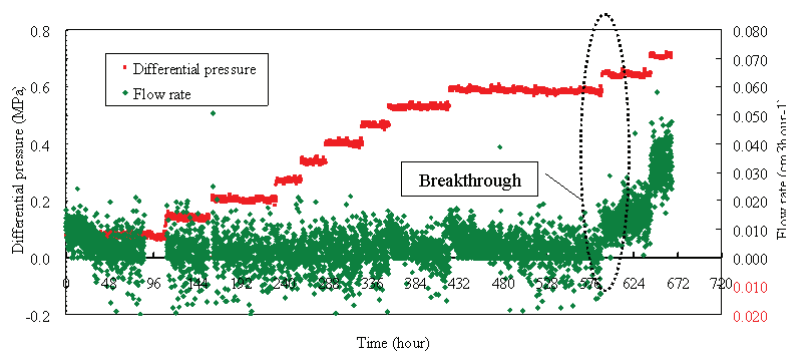
These obtained values with two approaches are summarized in Table 4.

Table 4. Summary of N<sub>2</sub> gas capillary threshold pressure with residual pressure and step-by-step approaches

Sample no	Water permeability	Residual pressure approach	Step-by-step approach
	Brine ( $\mu\text{D}$ )	$P_{\text{th}}$ N <sub>2</sub> /brine (MPa)	$P_{\text{th}}$ N <sub>2</sub> /brine (MPa)
1-b	1.80	0.37	0.9~1.0

### 3.3. Capillary threshold pressure with step-by-step approach for supercritical CO<sub>2</sub>

Capillary threshold pressure for supercritical CO<sub>2</sub> was measured with step-by-step approach and its test history is given in Figure 5. In this figure, differential pressure means inlet pressure of supercritical CO<sub>2</sub> minus backpressure.

Fig. 5. Test history of CO<sub>2</sub> capillary threshold pressure measurement with step-by-step approach (sample 1-b)

By using a backpressure pump, the downstream flow rate was monitored. Initially the flow rate showed instability and changed in negative or positive value. At 0.63 MPa of the differential pressure, it was observed a remarkable flow rate increase at outlet and recognized as a breakthrough. Supercritical CO<sub>2</sub> capillary threshold pressure of sample 1-b was considered between 0.58 and 0.63 MPa.

## 4. Discussions

### 4.1. Comparison between HPMT and step-by-step

The anticipated value for N<sub>2</sub> gas capillary threshold pressure from HPMT is 1.30 MPa, which is close to the value from step-by-step approach. In this experiment, two fragments showed very similar pore size distributions due to little heterogeneity of the sample. In such case, the anticipated capillary threshold pressure from HPMT would show similar results from step-by-step approach and might be valid.

On the other hand, there are also methodological shortcomings. HPMT approach is the lack of confining pressure and required for preparation procedure of drying [6]. Thus, it contains any alteration of sample's pore structure. For this reason, it would be necessary to measure capillary threshold pressures directly at *in situ* conditions.

#### 4.2. Comparison between step-by-step and residual pressure approach

As shown in Table 4 and in other papers [6] [7] [8], capillary threshold pressures with residual pressure approach are always lower than those with step-by-step approach. It might be considered that capillary threshold pressure measured by residual pressure approach is so-called ‘snap-off’ pressure. That is ‘the minimum capillary displacement pressure’ [9]. Residual pressure approach leads a systematic underestimation because of this snap-off phenomenon.

Additionally, sample 1-b in this study and sample 2 in literature [7] showed almost the same value of 0.9~1.0 MPa with step-by-step approach. However, values from residual pressure approach considerably differ from each other. The snap-off phenomenon would affect a value of capillary threshold pressure obtained by residual pressure approach and the magnitude of its influence would depend on the properties of samples, especially on the pore size distributions.

#### 4.3. Comparison between $N_2$ gas and supercritical $CO_2$

Table 5 shows results of measurements for  $N_2$  gas and supercritical  $CO_2$ . The second value is a  $P_c^{th}$  for supercritical  $CO_2$  recalculated from  $N_2$  gas capillary threshold pressure measured with step-by-step approach and the following equation;

$$P_{c(sc-CO_2/brine)}^{th} = P_{c(N_2/brine)}^{th} \frac{\sigma_{sc-CO_2/brine} \cos \theta_{sc-CO_2/brine}}{\sigma_{N_2/brine} \cos \theta_{N_2/brine}} \quad (3)$$

Again, values of Table 2 are used for recalculating by equation (3).

Table 5. Comparison of capillary threshold pressure measurements for different fluids

	Step-by-step approach	Recalculated value	Step-by-step approach
Sample no	$P_c^{th} N_2/brine$ (MPa)	$P_c^{th} CO_2/brine$ (MPa)	$P_c^{th} CO_2/brine$ (MPa)
1-b	0.9~1.0	Approximately 0.3	0.58~0.63

These results show that the measured value of capillary threshold pressure for supercritical  $CO_2$  is smaller by two-thirds than that for  $N_2$  gas. In literature [10], capillary threshold pressures measured for supercritical  $CO_2$  are smaller than those for  $N_2$  gas. These differences are likely due to differences in interfacial tension and contact angle.

The measured value for supercritical  $CO_2$  is about twice the recalculated value from measurement for  $N_2$  gas. In literature [11], similar results of difference between recalculated and measured values are shown and discussed that published data of interfacial tension for  $CO_2/brine$  system was underestimated in an experimental condition. It is also suggested that interfacial tension and contact angle have a lower impact on capillary threshold pressure than expressed in the Laplace equation.

Moreover in our study, the cumulative downstream flow volume was counted until breakthrough occurred. The downstream flow volume means the displacement volume of a wetting phase (brine) by a non-wetting phase (such as gas). In a supercritical  $CO_2$  experiment, the displacement volume was 6.9~12.1 % of pore volume which was larger than in  $N_2$  gas (5.4~6.4 % of pore volume). The difference of these displacement volumes might affect the difference of capillary threshold pressures between  $N_2$  gas and supercritical  $CO_2$ .

## 5. Conclusions

We have examined measurement methodologies of capillary threshold pressure and effects of injected fluid differences for selected pelitic rock samples. Main conclusions of this work are listed below.

1. The anticipated value for N<sub>2</sub> gas capillary threshold pressure from HPMI is 1.30 MPa, which is close to the value from step-by-step approach. In case of a sample with little heterogeneity, the anticipated value from HPMI might be valid.
2. Capillary threshold pressure with residual pressure approach is lower than that with step-by-step approach. However, in trying to conduct a step-by-step approach experiment, the derived value from residual pressure approach is utilizable. It could give an initial inlet N<sub>2</sub> gas pressure applied to step-by-step approach.
3. The supercritical CO<sub>2</sub> capillary threshold pressure measured with step-by-step approach is twice as large as the recalculated value from measurement for N<sub>2</sub> gas. More experimental studies are required to confirm this discrepancy.

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